Quantum thermodynamics: thermodynamics at the nanoscale

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A short introduction on quantum thermodynamics is given and three new topics are discussed: 1) Maximal work extraction from a finite quantum system. The thermodynamic prediction fails and a new, general result is derived, the "ergotropy". 2) In work extraction from two-temperature setups, the presence of correlations can push the effective efficiency beyond the Carnot bound. 3) In the presence of level crossing, non-slow changes may be more optimal than slow ones.

Thermodynamics originated in the nineteenth century as a science of engines. It took a while before it was understood that its laws originate from a molecular picture and, with it, the theory at that scale, quantum mechanics. Still, these efforts dealt with macroscopic systems.

When going to the limits of thermodynamics, one may wonder whether it exists for finite systems in the quantum regime, like few level atoms. At first sight, this seems a hopeless task. After all, there is nothing thermodynamical in the groundstate of the hydrogen atom, so why should there be such behavior for other finite systems? But let us notice that a thermodynamic setup deals with three parts: the system under consideration, a bath and a work source. The latter both have to remain extensive for having the proper physical meaning: the work source transfers high-graded energy (energy-without-entropy), while the bath transfers low-graded energy related to uncontrollable, thermalized degrees of freedom. In this setup there is a hope to understand thermodynamical laws directly from quantum mechanics.

One of the first question is then: can the energy U of the system S be uniquely identified, even though there is a non-small coupling to the bath? We have shown before that this can be done in two well known system+bath models: the Caldeira-Leggett model of a damped quantum particle in an external potential and the spin-boson model of a spin in the presence of a bath. For the Caldeira-Leggett model the Hamiltonian reads

$$\hat{H}_{\text{tot}} = \hat{H} + \hat{H}_B + \hat{H}_I, \quad \hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \tag{1}$$

$$\hat{H}_B = \sum_i \left[\frac{\hat{p}_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} \hat{x}_i^2 \right], \quad \hat{H}_I = -\sum_i c_i \hat{x}_i \hat{x}$$

and we choose a dense quasi-Ohmic spectrum

$$J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i) = \frac{\gamma \omega \Gamma^2}{\omega^2 + \Gamma^2} \tag{2}$$

where γ is the coupling or damping constant and Γ the 'Debye' cutoff frequency. Studying the Langevin dynamics, it was seen that for times larger than the inverse Debye frequency $1/\Gamma$, the unitary part of the equations of motion is given by the Hamiltonian[1,2]

$$\hat{H}_S = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) - \frac{1}{2} \gamma \Gamma \hat{x}^2. \tag{3}$$

For the harmonic case $\hat{V} = \frac{1}{2} b \hat{x}^2$ this implies an effective spring constant $a = b - \gamma \Gamma$ and $b > \gamma \Gamma$ or $a > 0$. This is exactly what is needed for stability of the overall system.

Now the internal energy is *uniquely* defined as $U = \text{tr} \hat{\rho} \hat{H}_S$, where $\hat{\rho}$ is the density matrix. A similar approach works[3] in the spin-boson model [1], the most important difference being that the (bare) Hamiltonian of the system already does the job.

The action of a *macroscopic work* source on the system S will be to make a parameter (for instance the effective mass m or the spring constant b) time-dependent. Therefore also the work đW done on S can be uniquely defined, as đ$W = \text{tr} \hat{\rho} \, \mathrm{d}\hat{H} = \text{tr} \hat{\rho} \left[(\partial \hat{H}/\partial m) \mathrm{d}m + (\partial \hat{H}/\partial b) \mathrm{d}b \right]$. It coincides with minus the energy change of the work-source.

Having these two ingredients, the first law is established, with the heat added to S: đ$Q = \mathrm{d}U - $đ$W$. This indicates that *Quantum Thermodynamics exists as a non-trivial subject.*

Now we can go to the second law. In the absence of a thermodynamic limit, its many formulations have different domains of validity. So one can no longer speak of *the* second law and, moreover, *entropy is a bad indicator* for a variety of reasons, see below.

In the PQE-2003 proceedings it was pointed out that[4]:

a). A generalized Thomson formulation (cycles cost work) is generally valid, provided the total system (including the bath and coupling to it) starts in gibbsian equilibrium[9]. An example of this case is to make a cyclic change in b. [2]

b). The Clausius inequality đ$Q \leq T \mathrm{d}S$ can be violated. This violation sets in at high T in subdominant $\hbar^2/T$ terms, and becomes strongest at $T = 0$, where $T\mathrm{d}S$ vanishes. The physical mechanism is the formation of a cloud of bath modes around the central system, as occurs for polarons and Kondo systems. Energy of this cloud can enter dU as heat. Experimental tests have been designed for quantum electronics [5] and quantum optics[3].

c). The rate of irreversible (non-adiabatic) work – sometimes called energy dispersion, when referring to the energy of the work source – may be negative at low enough T. This contrasts the classical case where it is equal to T times the rate of entropy production. As a result, starting out of equilibrium, a finite number of cycles could be designed where work is extracted from the bath [2,3].

1). The first new problem we treat here is one of the most known ones in thermodynamics: what is the maximal amount work that can be extracted from a non-equilibrium finite quantum system via cyclic processes[6]?

The maximal work-extraction problem is posed in the following way[7,8]. Let a system S be in an initial state with density matrix $\hat{\rho}_0$ and have Hamiltonian $\hat{H}$. Certain external fields are exerted on S in the time-interval $[0, \tau]$, which amount to a cyclic variation of the Hamiltonian: $\hat{H}(0) = \hat{H}(\tau) = \hat{H}$. As S is assumed to be thermally isolated (it moves under external fields and its own dynamics), the work W done by external sources is[7,8]

$$W = \text{tr}[\hat{H}\,\hat{\rho}_\tau] - \text{tr}[\hat{H}\,\hat{\rho}_0], \qquad (4)$$

where $\hat{\rho}_\tau$ is the state of S at the final moment τ. Work is extracted if $W < 0$, and the questions is what is the maximal amount $|W|$ which can be extracted, given $\hat{\rho}_0$ and H[7,8]. The standard answer[7,8] starts with postulating that the final state is in equilibrium at some temperature $T_f = 1/\beta_f$,

$$\hat{\rho}_\tau = \hat{\rho}_f = \frac{e^{-\beta_f \hat{H}}}{Z}, \qquad Z = \text{tr}\, e^{-\beta_f \hat{H}}. \qquad (5)$$

The work is then $W_{th} = U_f(S_f) - U_i$, where $U_f = \text{tr}\,[\hat{\rho}_f \hat{H}]$ is the final (average) energy as a function of final entropy $S_f = -\text{tr}\,\hat{\rho}_f \ln \hat{\rho}_f$, and U_i is the initial energy. Since in the final equilibrium state $dU_f/dS_f = T_f \geq 0$, for W_{th} to be minimal, one should keep S_f as small as possible. As the entropy of a thermally isolated system can only increase[7,8], the maximal amount of extracted work is achieved for conserved entropy: $S_f = S(0) = -\text{tr}\,\hat{\rho}_0 \ln \hat{\rho}_0$. This condition serves to determine T_f. Some known results follow: *i)* When comparing two different initial states $\hat{\rho}_0$ and $\hat{\sigma}_0$ of S having the same initial energy, more work can be extracted from that one which has lower entropy. *ii)* Conversely: if the maximal work extracted from $\hat{\rho}_0$ is larger than that from $\hat{\sigma}_0$, $\hat{\rho}_0$ had a lower entropy. *iii)* If there is an independent, uncorrelated system Ω ("spectator") with initial state $\hat{\omega}_0$ and Hamiltonian $\hat{H}_\omega$, then it just follows from the additivity of the entropy: $S(\hat{\rho}_0 \otimes \hat{\omega}_0) = S(\hat{\rho}_0) + S(\hat{\omega}_0)$, that more work can be extracted from $\hat{\rho}_0 \otimes \hat{\omega}_0$ than from $\sigma_0 \otimes \hat{\omega}_0$.

Maximal work extraction in quantum mechanics. It is now our purpose to solve the maximal work extraction problem directly from quantum mechanics, without involving any postulate. Let us start from the spectral resolutions

$$\hat{\rho}_0 = \sum_{j \geq 1} p_j |p_j\rangle\langle p_j|, \qquad \hat{H} = \sum_{k \geq 1} \varepsilon_k |\varepsilon_k\rangle\langle \varepsilon_k|, \quad (6)$$

where ε_k, p_k, $|\varepsilon_k\rangle$, $|p_k\rangle$ are the eigenvalues and orthonormal eigenvectors of $\hat{\rho}_0$ and H, respectively. We order the eigenvalues as

$$p_1 \geq p_2 \geq \cdots, \qquad \varepsilon_1 \leq \varepsilon_2 \leq \cdots \qquad (7)$$

Since S is assumed to be thermally isolated, its evolution is unitary: $\hat{\rho}_\tau = \hat{U}(\tau)\,\hat{\rho}_0\,\hat{U}^\dagger(\tau)$, with $i\hbar\,d\hat{U}(t)/dt = \hat{H}(t)\,\hat{U}(t)$.

The maximal extracted work $\mathcal{W} \equiv -W_{\max}$ was determined in[6]:

$$\mathcal{W} = U_0 - \sum_{k \geq 1} p_k\, \varepsilon_k, \quad U_0 = \sum_{i,k \geq 1} |\langle p_k | \varepsilon_i \rangle|^2\, \varepsilon_i p_k. \quad (8)$$

For $\mathcal{W}$, which depends only on the initial state and Hamiltonian, we coin the name *ergotropy*, from the ancient Greek, $\varepsilon\rho\gamma o\tau\rho o\pi\varepsilon\iota\alpha$ = work-transformation, transformation into work, ($\varepsilon\rho\gamma o\nu$, work; $\tau\rho o\pi\eta$, transformation, turn); in analogy to Clausius' *entropy*, ($\varepsilon\nu - \tau\rho o\pi\varepsilon\iota\alpha$, in-transformation).

It can be shown[6] that $\mathcal{W}_{th} \geq \mathcal{W} \geq 0$, and it is typically *not* equal to the thermodynamical expression $\mathcal{W}_{th} = U_i - U_f(S_f)$, because a unitary dynamics conserves all eigenvalues of $\hat{\rho}_0$ and not only its entropy. These additional conserved quantities are important for finite systems, *the thermodynamically optimal state is typically unreachable quantum mechanically.* For macroscopic systems the effect disappears or at least is expected to be very small – in the same way as energy is the only relevant constant of motion for a closed macroscopic system[7,8]. It thus holds that $\mathcal{W} \leq \mathcal{W}_{th}$[6].

The behavior of $\mathcal{W}$ can be rather different from that of its (unreachable) upper bound $\mathcal{W}_{th}$: *i)* states with a larger von Neumann entropy may produce more work; *ii)* introduction of a spectator system can invert the work-producing ability, that is, $\mathcal{W}(\hat{\sigma}) > \mathcal{W}(\hat{\rho})$ can be consistent with $\mathcal{W}(\hat{\omega} \otimes \hat{\sigma}) < \mathcal{W}(\hat{\omega} \otimes \hat{\rho})$. These and other related effects are discussed in detail in[6]. The standard thermodynamic behavior is still valid for finite systems, but only within the set of states that *majorize* one-another[6]. In that case the standard von Neumann is the proper indicator of work-providing ability.

2). *Work-extraction from a correlated two-temperature system may exceed the Carnot bound.* The most traditional object of work-extraction is a pair of equilibrium systems S_1 and S_2 with Hamiltonians $\hat{H}_1$ and $\hat{H}_2$, respectively. The total Hamiltonian is $\hat{H} = \hat{H}_1 + \hat{H}_2$ as S_1 and S_2 do not interact initially. Initially, at $t = 0$, S_1 and S_2 are in equilibrium states

$$\hat{\rho}_j(0) = \frac{e^{-\beta_j \hat{H}_j}}{Z_j}, \qquad Z_j = \text{tr}\, e^{-\beta_j \hat{H}_j}, \qquad j = 1, 2. \quad (9)$$

at temperatures $T_2 \geq T_1$. The total state of the baths $\hat{\rho}_0$ may be correlated: though $\hat{\rho}_{1,2} = \text{tr}_{2,1}\hat{\rho}_0$, it may hold that $\hat{\rho}_0 \neq \hat{\rho}_1 \otimes \hat{\rho}_2$. The maximal work $|W|$ is extracted from 0 till τ, while for $t > \tau$ one switches on for the system 1 (2) a weak interaction with a thermal bath at temperature T_1 (T_2). Due to this, both systems separately relax back to their original states $\hat{\rho}_1(0)$ and $\hat{\rho}_2(0)$ given by (9), though the total state need not return to $\hat{\rho}_0$. Changes of energies during this relaxation are completely attributed to heat. The heat Q_1 (Q_2) given by

the first (second) bath is:

$$Q_j = \text{tr}[\hat{H}_j \, \hat{\rho}_j(0)] - \text{tr}[\hat{H}_j \, \hat{\rho}_j(\tau)], \qquad j = 1, 2. \quad (10)$$

This is equal to the final energy of the bath minus the its initial value: the extracted work comes from the baths.

We now present a new, general theorem for this setup. For any system S with Hamiltonian $\hat{H}$ in a state $\hat{\rho}$ with energy $U = \text{tr}[\hat{\rho}\,\hat{H}]$, one defines the thermodynamic entropy $S_{\text{th}} \equiv \beta U - \ln Z$ as the von Neumann entropy of an equilibrium state $\hat{\rho}_{\text{eq}} = \exp[-\beta\hat{H}]/Z$ with the same energy. The temperature $T = 1/\beta$ follows from $dS_{\text{th}}/dU = \beta$. Since $d^2 S_{\text{th}}(U)/dU^2 = -1/\langle (\hat{H} - U)^2 \rangle < 0$, $S_{\text{th}}(U)$ is a monotonic and concave function. Now the identity $S_j(0) - S_j(\tau) = S_{\text{th}}(U_j(0)) - S_{\text{th}}(U_j(\tau))$ for $j = 1, 2$ implies, using Eq. (10) and that $f(x) - f(y) \geq f'(x)(x - y)$ for any concave function f,

$$S_{\text{th}}(U_j(0)) - S_{\text{th}}(U_j(\tau)) \geq \beta_j \left(U_j(0) - U_j(\tau) \right) = \beta_j Q_j. \tag{11}$$

Here the $S_j = -\text{tr}\,\hat{\rho}_j \ln \hat{\rho}_j$ are partial entropies, while $S = -\text{tr}\,\hat{\rho}_0 \ln \hat{\rho}_0$ is the total entropy. Together they define the non-negative correlation entropy[8]

$$S_{\text{corr}} = S_1 + S_2 - S \geq 0. \tag{12}$$

Considering this relation at $t = 0$ and $t = \tau$, using $S(\tau) = S(0)$ (unitarity), eliminating $Q_1 = |W| - Q_2$ (energy conservation), and noting $Q_2 \geq 0$ due to $T_2 \geq T_1$, one gets from (11) as efficiency of the cycle

$$\eta = \frac{|W|}{Q_2} \leq (1 - \frac{T_1}{T_2}) + \frac{T_1}{Q_2}(S_{\text{corr,i}} - S_{\text{corr,f}}). \tag{13}$$

If the initial state was factorized: $\hat{\rho}_0 = \hat{\rho}_1(0) \otimes \hat{\rho}_2(0)$, the maximal work extraction procedure will leave the final state in a factorized form, so $S_{\text{corr,i}} = S_{\text{corr,f}} = 0$, implying the maximal possible efficiency is the Carnot bound. For a factorized $\hat{\rho}_0$, the total state of S_1 and S_2 will return to it after interactions with the bath, so the whole procedure can be repeated. This is another formulation of the second law, but notice that our work extraction timescale, much smaller than the relaxation time of the bath, is not the most general one.

When the initial state is not factorized, the efficiency (13) is not bound by Carnot: correlations can be traded for efficiency. Such a result was found before in a setup of a laser cavity heated by a correlated three-level atom beam by Scully et al.[10] and discussed at PQE 2003.

3). *Non-adiabatic variations may exceed the thermodynamic work performance.* One of the formulations of the second law, the minimal work principle, states that work done on a thermally isolated equilibrium system is minimal for adiabatically slow (reversible) processes. Within the domain of finite quantum systems, it appears to be indeed generally valid provided the adiabatic energy levels do not cross. If level crossing does occur, this principle can be violated and optimal processes are neither adiabatically slow nor reversible. [14]

Formulation of the principle. Consider a quantum system S which is thermally isolated[7,8,11]: it moves according to its own dynamics and interacts with an external work source W. This interaction is realized via time-dependence of some parameters $R(t) = [R_1(t), ..., R_n(t)]$ of the system's Hamiltonian $\hat{H}(t) = \hat{H}[R(t)]$. They move along a certain trajectory $R(t)$ which at some initial time t_i starts from $R_i = R(t_i)$, and ends at R_f. The initial and final values of the Hamiltonian are $\hat{H}_i = \hat{H}[R_i]$ and $\hat{H}_f = \hat{H}[R_f]$, respectively. Initially S is assumed to be in equilibrium at temperature $T = 1/\beta$, that is, S is described by a density operator:

$$\hat{\rho}(t_i) = \exp[-\beta\hat{H}_i]/Z_i, \qquad Z_i = \text{tr}\, e^{-\beta\hat{H}_i}. \tag{14}$$

One considers various processes which start from the same equilibrium state (14) with R moving between R_i and R_f along a trajectory $R(t)$. The statement of the minimum work-principle then reads[7,8,11]

$$W \geq W_{\text{ad}} : \tag{15}$$

The actual work W done on S when moving along the trajectory $R(t)$ is not smaller than the work W_{ad} done during the adiabatically slow variation between the same initial and final values R_i and R_f and along the same trajectory $R(t)$. By adiabatically slow we mean a process which is realized with homogeneously vanishing velocity and which thus takes very long time $t_f - t_i$, much longer than the proper characteristic time of S. For thermally isolated systems S adiabatically slow processes are reversible. This is standard if S is macroscopic[7,8,11], and was shown to be true also in the finite domain, where the definition of reversibility extends unambiguously[14] (i.e., without using entropy).

Eq. (15) is a statement on optimality: if the purpose of the external source W is to extract work from S, then the actual work W is negative, and to make it as negative as possible one proceeds with very slow velocity. On the other hand, if during some operation the work has to be put into S, that is W has to be positive, one tends to minimize its amount, and again operates adiabatically slow. In macroscopic thermodynamics the minimum work principle is derived[7,8] from certain axioms which ensure that, within the domain of their applicability, this principle is equivalent to other formulations of the second law. Derivations in the context of statistical thermodynamics are presented in[12,13].

The minimal work principle for macroscopic systems is proven in two steps: first one establishes an inequality between the work and the free energy difference, while in the second step one uses macroscopic features of S to connect it with the adiabatic work. One starts with the relative entropy $\text{tr}[\hat{\rho}(t_f) \ln \hat{\rho}(t_f) - \hat{\rho}(t_f) \ln \hat{\rho}_{\text{eq}}(\hat{H}_f)]$ between the final state $\hat{\rho}(t_f)$ and an equilibrium state $\hat{\rho}_{\text{eq}}(\hat{H}_f) = \exp[-\beta\hat{H}_f]/Z_f$, $Z_f = \text{tr}\, e^{-\beta\hat{H}_f}$. It has the same temperature $T = 1/\beta$ as the initial state $\hat{\rho}(t_i)$, but corresponds to the final Hamiltonian $\hat{H}_f$. As follows from

unitarity, $\text{tr}[\hat{\rho}(t_\text{f}) \ln \hat{\rho}(t_\text{f})] = \text{tr}[\hat{\rho}(t_\text{i}) \ln \hat{\rho}(t_\text{i})]$. Combined with (14, 4) and non-negativity of relative entropy[8], this yields:

$$W \geq F(\hat{H}_\text{f}) - F(\hat{H}_\text{i}) \equiv T \ln \text{tr}[e^{-\beta \hat{H}_\text{i}}] - T \ln \text{tr}[e^{-\beta \hat{H}_\text{f}}]),$$

where $F(\hat{H}_\text{i})$ and $F(\hat{H}_\text{f})$ are the free energies corresponding to $\hat{\rho}(t_\text{i})$ and $\hat{\rho}_\text{eq}(\hat{H}_\text{f})$, respectively. There are several classes of macroscopic systems for which one can show that the free energy difference $F(\hat{H}_\text{f}) - F(\hat{H}_\text{i})$ indeed coincides with the adiabatic work[2,12,13].

Finite systems.[14] For an arbitrary N-level quantum system S, Eq. (16) does not have the physical meaning we need, since in general $F(\hat{H}_\text{f}) - F(\hat{H}_\text{i})$ has no reason to coincide with the the adiabatic work needed in (15). Therefore, one needs an independent, possibly general, proof of (15). In [14] we present one, starting from the quantum evolution equations and using ideas from [9].

Let the spectral resolutions of $\hat{H}(t)$ and $\hat{\rho}(t_\text{i})$ be

$$\hat{H}(t) = \sum_{k=1}^{N} \varepsilon_k(t)|k,t\rangle\langle k,t|, \quad \langle k,t|n,t\rangle = \delta_{kn}, \quad (16)$$

$$\hat{\rho}(t_\text{i}) = \sum_{k=1}^{N} p_k |k,t_\text{i}\rangle\langle k,t_\text{i}|, \quad p_k = \frac{e^{-\beta\varepsilon_k(t_\text{i})}}{\sum_n e^{-\beta\varepsilon_n(t_\text{i})}}. \quad (17)$$

The ordering (7) is satisfied at $t = t_\text{i}$. For $t_\text{i} \leq t \leq t_\text{f}$ we expand on the complete set $|n,t\rangle$: $\hat{U}(t)|k,t_\text{i}\rangle = \sum_{n=1}^{N} a_{kn}(t) \, e^{-\frac{i}{\hbar}\int_{t_\text{i}}^{t} \text{d}t' \, \varepsilon_n(t')} |n,t\rangle$, and uses (22, 4) to get:

$$W - W_\text{ad} = \sum_{m=1}^{N-1} [\varepsilon_{m+1}(t_\text{f}) - \varepsilon_m(t_\text{f})] \, \Theta_m, \quad (18)$$

$$\Theta_m \equiv \sum_{n=1}^{m} \sum_{k=1}^{N} p_k (\, |\tilde{a}_{kn}(t_\text{f})|^2 - |a_{kn}(t_\text{f})|^2). \quad (19)$$

Assume now that the ordering (7) is kept at $t = t_\text{f}$:

$$\varepsilon_1(t_\text{f}) \leq ... \leq \varepsilon_N(t_\text{f}). \quad (20)$$

If energy levels did not cross each other, i.e. $\varepsilon_{k+1}(t) - \varepsilon_k(t)$ did not change its sign as a function of t for $t_\text{i} \leq t \leq t_\text{f}$, then (20) is implied by (7). According to non-crossing rule[15], if only one independent parameter of the Hamiltonian $\hat{H}(t)$ is varied, the above condition is satisfied for any discrete-level quantum system: level-crossing, even if it happens in model-dependent calculations or due to approximate symmetry, does not survive arbitrary small perturbation and is substituted by avoided crossing. In that case the standard adiabatic theorem of quantum mechanics[16] leads to

$$\tilde{a}_{kn}(t_\text{f}) = \delta_{kn} \quad (21)$$

It follows from $|a_{kn}(t_\text{f})|^2 = |\langle n,t_\text{f}|\hat{U}|k,t_\text{i}\rangle|^2$ that

$$\sum_{k=1}^{N} |a_{kn}(t_\text{f})|^2 = \sum_{n=1}^{N} |a_{kn}(t_\text{f})|^2 = 1. \quad (22)$$

Combined with (7, 21) this brings $\Theta_m \geq 0$. Together with Eqs. (7, 20) this proves the minimum work principle (15) for finite systems, without requiring a connection with the free energy difference[14].

Level crossing. What happens if the adiabatic energy levels cross, i.e. (20) is not valid? As an example we consider a spin-$1/2$ particle with Hamiltonian [14]

$$\hat{H}(t) = h_1(s)\hat{\sigma}_1 - h_3(s)\hat{\sigma}_3, \qquad s = t/\tau, \quad (23)$$

where $\hat{\sigma}_1$ and $\hat{\sigma}_3$ are the corresponding Pauli matrices, and s is the reduced time with τ being the characteristic time-scale. The external magnetic fields h_1 and h_3 vary smoothly in time. Assume that *i)* for $s \to s_\text{i} < 0$ and for $s \to s_\text{f} > 0$, $h_1(s)$ and $h_3(s)$ go to constant values sufficiently fast; *ii)* for $s \to 0$ one has: $h_1(s) \simeq \alpha_1 s^2$, $h_3(s) \simeq -\alpha_3 s$, where α_1 and $\alpha_3 > 0$ are constants. *iii)* $h_1(s)$ and $h_3(s)$ are non-zero for all s, $s_\text{i} \leq s \leq s_\text{f}$, except $s = 0$. For large τ one gets[14]

$$|a_{12}(t_\text{f})|^2 = \frac{\pi\hbar\alpha_1^2}{4\tau\alpha_3^3}, \quad (24)$$

which for $\tau \to \infty$ is in accordance with the adiabatic theorem (21). From (18) we have $W - W_\text{ad} = [\varepsilon_2(t_\text{f}) - \varepsilon_1(t_\text{f})]\Theta_1$. Using $\Theta_1 = (p_1 - p_2)|a_{12}(t_\text{f})|^2 > 0$ we find, because of the level crossing, $W - W_\text{ad} = -|\varepsilon_2(t_\text{f}) - \varepsilon_1(t_\text{f})|\Theta_1 < 0$, thus confirming the violation of the minimum work principle. Eq. (24) also shows that the role of the proper internal characteristic time is $\hbar\alpha_1^2/\alpha_3^3$.

In the above two-level example one crossing was sufficient to violate (15) with practically any non-adiabatic variation which produces $\Theta_1 > 0$. For a many-level S having two of its levels crossed, any non-adiabatic variation will not do anymore, as only one term in the RHS of (18) will be negative. However, for quasi-adiabatic variations – and provided $\hat{H}(t)$ is analytic – the transition probabilities between non-crossing levels are exponentially small[16,17], while as we seen it has power-law smallness for the two crossing levels. For this situation one can neglect in (18) the contribution from non-crossing levels, and the problem is reduced to the two-level situation. The same concerns macroscopic systems which have at least two discrete levels at the bottom of a continuous spectrum, whenever for low temperatures these levels decouple from the rest of the spectrum.

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